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Combining $AlCl_3 \cdot 6H_2O$ and an ionic liquid to prepare chlorohydrin esters from glycerol

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ABSTRACT

We describe here the first example in which glycerol has been transformed into chlorohydrin esters using an ionic liquid and hydrated aluminium chloride. The method avoids using Crown-18 ether, which was needed to obtain a similar yield when KCl was used. Alkyl and aryl acids can be used, although yields are very dependent on the carboxylic acid used.

Glycerol is considered a low-cost, renewable feedstock that is a co-product of the biodiesel process.[1] Recently, new procedures have been patented to convert this compound to a mixture of chlorohydrin esters, commercial compounds with wide applications.[2]

We have already developed a direct methodology to prepare chlorohydrin esters from polyols. The method consists of a one-pot esterification–chlorination reaction, in which chlorotrimethylsilane acts as a solvent and reagent. Using this methodology, dichloropropyl esters can be obtained by an esterification–substitution reaction from 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane (solketal), a monoketal from glycerol.[3] Dichloropropyl palmitate could be also obtained in low yields from glycerol and hydrochloric acid.[4] To avoid the use of chlorotrimethylsilane, we have developed a new friendly one-pot halohydrin ester synthesis using potassium halides (KX) as the halogen source in ionic liquids ([BMIM][PF_6]) in the presence of Crown-18 ether.[5] Using this methodology, several diols and carboxylic acids were transformed to the corresponding halohydrin esters.

As a continuation of our work, we report here that glycerol undergoes an esterification–substitution reaction with a carboxylic acid to give the corresponding chlorohydrin ester in 48 h with [BMIM][PF_6] as a solvent and $AlCl_3 \cdot 6H_2O$ as a source of chlorine.[6] The corresponding 1,3-dichloro-2-propyl ester **3** (Fig. 1) is the main regioisomer. When palmitic acid is chosen as a model reagent, it is observed that yields can be maintained by using $AlCl_3 \cdot 6H_2O$ instead of KCl[7] (entry a), avoiding the use of crown ether as was proposed in our previous work (Table 1).

To the best of our knowledge, this reaction represents the first example of dichlorohydrin ester synthesis from glycerol using an ionic liquid and metal halide as chloride source. Hydrated aluminium chloride is much easier to handle than the corresponding anhydrous $AlCl_3$ and Friedel–Craft-like reactions are avoided.

The importance of these results particularly relates to: (i) the transformation of a renewable material to valuable compounds,

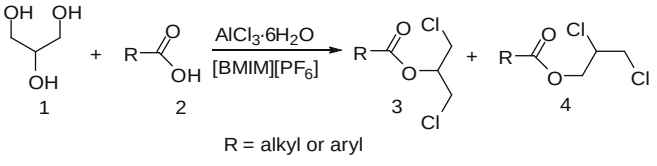

Figure 1. Preparation of dichloropropyl esters from glycerol and a carboxylic acid.

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Table 1
Dichoropropyl esters **3a–p:4a–p** produced from glycerol and carboxylic acid in [BMIM][PF_6]

Entry	R	Conditions	Ratio **3**:**4**[a]	Yield[b] (%)
a	$CH_3(CH_2)_{14}$	KCl (5 mequiv), 18-Crown ether[c]	94:6	83
a	$CH_3(CH_2)_{14}$	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	93:7	80
b	$CH_3(CH_2)_4CH{=}CH(CH_2)_{10}$	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	95:5	73
c	$CH_3(CH_2)_{13}$	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	95:5	76
d	$CH_3(CH_2)_{10}$	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	96:4	56
e	$CH_3(CH_2)_6$	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	70:30	28
f	2-Furoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	68:32	8
f	2-Furoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	68:32	48
g	2-Thiophencarboxoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	81:19	13
g	2-Thiophencarboxoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	81:19	50
h	Benzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	78:22	25
h	Benzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	78:22	87
i	Cinnamyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	68:32	9
i	Cinnamyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	68:32	36
j	Salicyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	86:14	6
j	Salicyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	86:14	21
k	2-Chlorobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	83:13	19
k	2-Chlorobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	83:13	64
l	3-Aminobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	—	—[e]
l	3-Aminobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	88:12	41[e]
m	3-Nitrobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	95:5	9
m	3-Nitrobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	95:5	88
n	3,5-Dinitrobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	—	—
n	3,5-Dinitrobenzoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	55:45	56
o	1-Naphthoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	72:28	16
o	1-Naphthoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	72:28	24
p	2-Naphthoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	75:25	30
p	2-Naphthoyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	75:25	62
q	Picolyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[c]	—	—[e]
q	Picolyl	$AlCl_3{\cdot}6H_2O$ (2 mequiv)[d]	—	—[e]

[a] Calculated by ^{1}H NMR considering signals at $\delta = 5.19$ ppm for **3** and $\delta = 4.22$ ppm for **4**.
[b] Yield calculated by ^{1}H NMR using 1,4-dichlorobenzene for aliphatic acids and 1,4-dioxane for aromatic and heteroaromatic acids.
[c] Crude reaction mixture was extracted with hexane.
[d] Crude reaction mixture was dissolved in water and extracted with ethyl acetate.
[e] After careful neutralization with solid sodium bicarbonate.

(ii) the use of a handy chloride salt as chloride source and (iii) the use of an ionic liquid (IL) as solvent.

Table 1 shows the different regioisomeric ratios obtained depending on the carboxylic acid used. Nevertheless, regioisomer **3** is always the main compound obtained. Kinetic control is proposed to explain the predominance of this regioisomer. This hypothesis is in agreement with several similar reactions.[8] The ratio dependence upon the carboxylic acid used could be explained considering the charge density at the carbon of the carboxylic group.[9] Nevertheless, 3-nitrobenzoic acid and oleic acid gave the highest **3**:**4** ratio whereas 3,5-nitrobenzoic acid gave the lowest **3**:**4** ratio. Ionic liquids can produce different electrostatic environments, which can significantly affect a given reaction. Furthermore, ionic liquids are able to give π–π and π–cation interactions that in some cases may significantly affect the reactivity in these solvent media.[10] Bearing in mind the putative ionic intermediates present in these processes,[3] ions constituting ionic liquids could induce different effects depending on the starting carboxylic acid. Opposing effects on the rate of reaction of the substrate have been described for unimolecular substitution processes in presence of ionic liquids. Addition of different amounts of ionic liquid to the reaction mixture, favoured in different extents the reaction in terms of activation enthalpy whereas disfavoured it in terms of activation entropy.[11] These facts could explain that the regioisomeric ratios were very sensitive to the chemical structure of the reagents. Yields are also rather dependent on the carboxylic acid used. For aliphatic acids, the highest yield was obtained for palmitic acid. Acids with shorter chain lengths showed lower yields. For aromatic and heteroaromatic acids, yields range from high (benzoic and 3-nitrobenzoic acids) to low (salicylic, cinnamic and 1-naphthoic acids) (Table 1). The reaction is compatible with C=C bonds, aromatic amino and hydroxyl groups. Only picolinic acid (**2q**) did not give the desired compounds in the described conditions.

These results are similar to those obtained in our previous work when several diols were assayed.[5] The fact that these reactions in ionic liquids are very sensitive to the chemical structure of the reagents can be used again to explain these results.[12] Consequently, large aliphatic acids (oleic, palmitic and pentadecanoic acids) and some small aromatic acids will be the best acids for carrying out this reaction in [BMIM][PF_6]. Moreover, the recovery of the resulting esters from the reaction mixture with solvents such as hexane seems more difficult when aromatic acids are used (Table 1). The addition of water at the end of the reaction, followed by extraction with ethyl acetate seems to overcome this second fact.

In conclusion, we have described the first example in which glycerol has been transformed to chlorohydrin esters using an ionic liquid and hydrated aluminium chloride. The described method avoids using Crown-18 ether needed to obtain satisfactory yields when KCl is used. Alkyl and aryl acids can be used, although yields are very dependent on the carboxylic acid used. Aminoaromatic acids seem to be compatible with the reaction conditions used.

Acknowledgement

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6. *Experimental procedure*: A mixture of carboxylic acid (1 mequiv), glycerol (2 mequiv) and hydrated aluminium chloride (2 mequiv) and [BMIM][PF_6] (2.5 g) were stirred in a 10 mL reactor for 48 h at 100 °C. The crude reaction mixture was extracted with hexane (3 × 2 mL) while stirring in a circular shaker placed into an oven for 30 min at 40 °C. Crude reaction mixtures from aromatic and heteroaromatic acids were also dissolved in water and extracted with ethyl acetate (3 × 20 mL). The upper phase was recovered and dried over anhydrous sodium sulfate. Organic solutions were filtered and evaporated to dryness. Yields were determined using ^{1}H NMR with either 1,4-dichlorobenzene or 1,4-dioxane as internal standard (see Table 1).
1,3-Dichloro-2-propyl palmitate (**3a**): ^{1}H NMR ($CDCl_3$), δ: 5.18 (quin, $J = 5.2$ Hz, 1H, O–C*H*), 3.73 (m, 4H, 2 CH_2–Cl), 2.37 (t, $J = 7$ Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 1.65 (m, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.26 (m, 24H, CH_2), 0.88 (t, $J = 7$ Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 172.7 (C=O), 71.5 (O–CH), 42.5 (CH_2–Cl), 34.1 ($CH_{2\ (\alpha)}$ (C=O)), 31.9 (CH_2–CH_2–CH_3), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0 (CH_2), 24.8 ($CH_{2\ (\beta)}$ (C=O)), 22.7 (CH_2-CH_3), 14.1 (CH_3).
1,3-Dichloro-2-propyl oleate (**3b**): ^{1}H NMR ($CDCl_3$), δ: 5.35 m, 2H, C*H*=C*H*), 5.18 (quin, $J = 5.1$ Hz, 1H, O–C*H*), 3.74 (dd, $J_1 = 11.6$ Hz, $J_2 = 2$ Hz, 4H, 2 CH_2–Cl), 2.36 (t, $J = 7.4$ Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 2.0 (m, 4H, CH_2–CH=), 1.68 (m, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.26 (m, 18H, CH_2), 0.88 (t, $J = 7.0$ Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 172.9 (C=O), 130.2, 129.9 (CH=CH), 71.7 (O–CH), 42.7 (CH_2–Cl), 34.3 ($CH_{2\ (\alpha)}$ (C=O)), 32.1 (CH_2–CH_2–CH_3), 30.0, 29.9, 29.7, 29.5, 29.4, 29.3, (CH_2), 26.7 (CH_2–CH=CH–CH_2), 25.0 ($CH_{2\ (\beta)}$ (C=O)), 22.9 (CH_2-CH_3), 14.3 (CH_3). HRMS (EI+) calculated for $C_{11}H_{20}O_2Cl_2$: 392.2249. Found: 392.2247.
1,3-Dichloro-2-propyl pentadecanoate (**3c**): ^{1}H NMR ($CDCl_3$), δ: 5.18 (quin, $J = 5.2$ Hz, 1H, O–C*H*), 3.74 (dd, $J_1 = 5.4$ Hz, $J_2 = 2$ Hz, 4H, 2 CH_2–Cl), 2.36 (t, $J = 7.4$ Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 1.64 (m, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.25 (m, 22H, CH_2),

0.87 (t, J = 6.9 Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 173.0 (C=O), 71.7 (O–CH), 42.7 (CH_2–Cl), 34.4 ($CH_{2\ (\alpha)}$ (C=O)), 32.2 (CH_2–CH_2–CH_3), 29.9, 29.8, 29.7, 29.6, 29.4, 29.3 (CH_2), 25.1 ($CH_{2\ (\beta)}$ (C=O)), 22.9 (CH_2-CH_3), 14.4 (CH_3). HRMS (EI+) calculated for $C_{11}H_{20}O_2Cl_2$: 352.1936. Found: 352.1932.

1,3-Dichloro-2-propyl laureate (**3d**): ^{1}H NMR ($CDCl_3$), δ: 5.18 (quin, J = 5.2 Hz, 1H, O–CH), 3.73 (dd, J_1 = 5.4 Hz, J_2 = 2 Hz, 4H, 2 CH_2–Cl), 2.37 (t, J = 7 Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 1.65 (m, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.26 (m, 24H, CH_2), 0.88 (t, J = 7 Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 173.0 (C=O), 71.7 (O–CH), 42.7 (CH_2–Cl), 34.3 ($CH_{2\ (\alpha)}$ (C=O)), 32.1 (CH_2–CH_2–CH_3), 29.8, 29.6, 29.5, 29.4, 29.3, (CH_2), 25.1 ($CH_{2\ (\beta)}$ (C=O)), 22.9 (CH_2-CH_3), 14.3 (CH_3).

1,3-Dichloro-2-propyl caprylate (**3e**): ^{1}H NMR ($CDCl_3$), δ: 5.12 (quin, J = 5.1 Hz, 1H, O–CH), 3.74 (dd, J_1 = 5.5 Hz, J_2 = 2.0 Hz, 4H, 2 CH_2–Cl), 2.34 (t, J = 7.8 Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 1.63 (quin, J = 7.4 Hz, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.29 (m, 8H, CH_2), 0.87 (t, J = 7.0 Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 173.0 (C=O), 72.0 (O–CH), 42.0 (CH_2–Cl), 34.4 ($CH_{2\ (\alpha)}$ (C=O)), 32.1 (CH_2–CH_2–CH_3), 29.5 (CH_2), 25.0 ($CH_{2\ (\beta)}$ (C=O)), 22.5 (CH_2-CH_3), 14.5 (CH_3).

1,3-Dichloro-2-propyl 2-furoate (**3f**): ^{1}H NMR ($CDCl_3$), δ: 7.62 (m, CH_{ar}), 7.26 (dt, J_1 = 3.5 Hz, J_2 = 0.8 Hz, 1H, CH_{ar}), 6.53 (m, 1H, CH_{ar}), 5.39 (quin, J = 5.1 Hz, 1H, O–CH), 3.85 (d, J = 5.6 Hz, 4H, CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 156.9 (C=O), 146.5 (CH_{ar}), 143.7 (CH_{ar}–C=O), 119.8, 112.1 (CH_{ar}), 72.3 (O–CH), 43.1 (CH_2–Cl).

1,3-Dichloro-2-propyl 2-thiophencarboxylate (**3g**): ^{1}H NMR ($CDCl_3$), δ: 7.79 (dd, J_1 = 3.9 Hz, J_2 = 1.2 Hz, 1H, CH_{ar}), 7.55 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1H, CH_{ar}), 7.06 (dd, J_1 = 5.0 Hz, J_2 = 3.9 Hz, 1H, CH_{ar}), 5.31 (quin, J = 5.1 Hz, 1H, O–CH), 3.80 (d, J = 5.1 Hz, 4H, CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 161.1 (C=O), 144.8 (CH_{ar}), 143.8 (CH_{ar}–C=O), 122.5, 118.1 (CH_{ar}), 72.2 (O–CH), 42.8 (CH_2–Cl).

1,3-Dichloro-2-propyl benzoate (**3h**): ^{1}H NMR ($CDCl_3$), δ: 8.00 (m, 1H, $CH_{ar\ (\alpha)}$ (C=O)), 7.53 (m, 1H, CH_{ar}), 7.39 (m, 2H, CH_{ar}), 5.36 (quin, J = 5.3 Hz, 1H, O–CH), 3.82 (m, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 163.4 (C=O), 131.7,127.9, 127.2, 126.6 (C_{ar}), 70.1 (O–CH), 40.5 (CH_2–Cl).

1,3-Dichloro-2-propyl cinnamate (**3i**): ^{1}H NMR ($CDCl_3$), δ: 7.73 (d, J = 15.6 Hz, 1H, CH_{ar}), 7.48 (m, 2H, 2 CH_{ar}), 7.34 (m, 3H, 2 CH_{ar}, Ph–CH=CH), 6.41 (m, 1H, Ph–CH=CH), 5.25 (quin, J = 5.1 Hz, 1H, O–CH), 3.76 (d, J = 5.5 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 165.9 (C=O), 146.7 (Ph–CH=CH), 134.2 (C_{ar}), 130.9, 129.2, 128.5 (CH_{ar}), 117.0 (Ph–CH=CH), 71.9 (O–CH), 42.7 (CH_2–Cl).

1,3-Dichloro-2-propyl salicylate (**3j**): ^{1}H NMR ($CDCl_3$), δ: 7.81 (dd, J_1 = 8.2 Hz, J_2 = 1.7 Hz, 1H, CH_{ar}), 7.50 (m, 1H, CH_{ar}), 6.95 (d, J = 7.5 Hz, 1H, CH_{ar}), 6.80 (m, 1H, CH_{ar}), 5.39 (quin, J = 5.1 Hz, 1H, O–CH), 3.82 (d, J = 5.5 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 169.1 (C=O), 162.1 (C_{ar}-OH), 136.7, 130.3, 119.7, 117.9, 111.8 (CH_{ar}), 72.7 (O–CH), 42.5 (CH_2–Cl).

1,3-Dichloro-2-propyl 2-chlorobenzoate (**3k**): ^{1}H NMR ($CDCl_3$), δ: 7.88 (m, 1H, CH_{ar}), 7.47 (td, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 2H, CH_{ar}), 7.35 (m, 1H, CH_{ar}), 5.44 (quin, J = 5.2 Hz, 1H, O-CH), 3.89 (d, J = 5.5 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 164.5 (C=O), 134.4 (C_{ar}–OH), 133.4, 131.9, 131.5, 129.1, 126.9 (C_{ar}), 72.9 (O–CH), 42.5 (CH_2–Cl).

1,3-Dichloro-2-propyl 3-aminobenzoate (**3 l**): ^{1}H NMR ($CDCl_3$), δ: 5.38 (quin, J = 5.0 Hz, 1H, O–CH), 3.90 (d, 4H, J = 5.1 Hz, 2 CH_2–Cl). ^{13}C RMN (MeOD), δ: 166.1 (C=O), 148.4 (C_{ar}-NH_2), 130.1 (C_{ar}-C=O), 129.0, 119.9, 118.8, 115.7 (CH_{ar}), 72.6 (O–CH), 42.6 (CH_2–Cl). HRMS (EI+) calculated for $C_{11}H_{20}O_2Cl_2$: 247.0167. Found: 247.0162.

1,3-Dichloro-2-propyl 3-nitrobenzoate (**3 m**): ^{1}H NMR ($CDCl_3$), δ: 8.87 (s, 1H, CH_{ar}), 8.42 (dd, J_1 = 25.0 Hz, J_2 = 8.2 Hz, 2H, CH_{ar}), 7.69 (t, J = 8.2 Hz, 1H, CH_{ar}), 5.48 (quin, J = 5.1 Hz, 1H, O–CH), 3.90 (d, J = 5.5 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 163.8 (C=O), 151.1 (C_{ar}–NO_2), 134.7 (C_{ar}–C=O), 130, 129.8, 122.7 (CH_{ar}), 73.3 (O–CH), 42.5 (CH_2–Cl).

1,3-Dichloro-2-propyl 3,5-dinitrobenzoate (**3n**): ^{1}H NMR ($COCD_6$), δ: 9.17 (t, J = 2.1 Hz 1H, CH_{ar}), 9.10 (d, J = 2.1 Hz, 2H, CH_{ar}), 5.67 (quin, J = 5.1 Hz, 1H, O–CH), 4.11 (d, J = 5.1 Hz, 4H, CH_2–Cl). ^{13}C RMN ($COCD_6$), δ: 164.4 (C=O), 149.1 (C_{ar}–NO_2), 134.3 (C_{ar}–C=O), 128.0, 122.8 (CH_{ar}), 76.3 (O–CH), 43.5 (CH_2–Cl).

1,3-Dichloro-2-propyl 1-naphthoate (**3o**): ^{1}H NMR ($CDCl_3$), δ: 8.93 (dd, J_1 = 8.8 Hz, J_2 = 0.8 Hz, 1H, CH_{ar}), 8.28 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H, CH_{ar}), 8.07 (d, J = 8.4 Hz, 1H, CH_{ar}), 7.91 (d, J = 7.6 Hz, 1H, CH_{ar}), 7.65 (m, 1H, CH_{ar}), 7.54 (m, 2H, 2 CH_{ar}), 5.54 (quin, J = 4.8 Hz, 1H, O–CH), 3.96 (d, J = 4.8 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 166.3 (C=O), 134.4, 134.1, 131.6, 131.2, 128.9, 128.4, 126.6, 125.9, 125.8, 124.8 (CH_{ar}), 72.4 (O–CH), 42.8 (CH_2–Cl).

1,3-Dichloro-2-propyl 2-naphthoate (**3p**): ^{1}H NMR ($CDCl_3$), δ: 8.58 (s, 1H, CH_{ar}), 8.01 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H, CH_{ar}), 7.92 (d, J = 8.4 Hz, 1H, CH_{ar}), 7.84 (d, J = 8.8 Hz, 1H, CH_{ar}), 7.83 (d, J = 8 Hz, 1H, CH_{ar}), 7.53 (m, 2H, 2 CH_{ar}), 5.44 (quin, J = 4.8 Hz, 1H, O–CH), 3.88 (d, J = 4.8 Hz, 4H, 2 CH_2–Cl). ^{13}C RMN ($CDCl_3$), δ: 165.8 (C=O), 136.0, 132.7, 131.9, 129.7, 128.9, 128.6, 128.0, 127.1, 126.6, 125.4 (CH_{ar}), 72.4 (O–CH), 42.7 (CH_2–Cl).

7. *Experimental procedure*. A mixture of palmitic acid (1 mequiv), glycerol (2 mequiv), Crown-18 ether (0.125 mequiv, 10% mol), potassium chloride (5 mequiv) and [BMIM][PF_6] (2.5 g) was stirred in a 10-mL reactor for 48 h at 100 °C. The crude reaction mixture was extracted with hexane (3 × 2 mL) while stirring in a circular shaker placed into an oven for 30 min at 40 °C. The upper phase was recovered and dried over anhydrous sodium sulfate. Organic solution was filtered and evaporated to dryness. Yield was determined using ^{1}H NMR with 1,4-dichlorobenzene[13] as internal standard.

1,3-Dichloro-2-propyl palmitate (**3a**): ^{1}H NMR ($CDCl_3$), δ: 5.18 (quin, J = 5.2 Hz, 1H, O–CH), 3.73 (m, 4H, 2 CH_2–Cl), 2.37 (t, J = 7 Hz, 2H, $CH_{2\ (\alpha)}$ (C=O)), 1.65 (m, 2H, $CH_{2\ (\beta)}$ (C=O)), 1.26 (m, 24H, CH_2), 0.88 (t, J = 7 Hz, 3H, CH_3). ^{13}C RMN ($CDCl_3$), δ: 172.7 (C=O), 71.5 (O–CH), 42.5 (CH_2–Cl), 34.1 ($CH_{2\ (\alpha)}$ (C=O)), 31.9 (CH_2–CH_2–CH_3), 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0 (CH_2), 24.8 ($CH_{2\ (\beta)}$ (C=O)), 22.7 (CH_2–CH_3), 14.1 (CH_3).

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